

11:49:21

OCA PAD INITIATION - PROJECT HEADER INFORMATION

10/10/88

Active

Project #: E-25-619
Center # : R6596-OA0

Cost share #:
Center shr #:

Rev #: 0
OCA file #:
Work type : RES
Document : PO
Contract entity: GTRC

Contract#: AX-0857216
Prime #: DOE AC09-76SR00001

Mod #:

Subprojects ? : N
Main project #:

Project unit: ME
Project director(s):
EICHHOLZ G G ME

Unit code: 02.010.126

Sponsor/division names: SAVANNAH RIVER LABORATORY
Sponsor/division codes: 240

/ E I DUPONT DE NEMOURS CO
/ 004

Award period: 880902 to 890602 (performance) 890602 (reports)

Sponsor amount	New this change	Total to date
Contract value	25,506.00	25,506.00
Funded	25,506.00	25,506.00
Cost sharing amount		0.00

Does subcontracting plan apply ? : N

Title: ABSORPTION OF ACTINIDES ON SRP SOIL

PROJECT ADMINISTRATION DATA

OCA contact: Steven K. Watt

894-4820

Sponsor technical contact

Sponsor issuing office

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Security class (U,C,S,TS) : U

ONR resident rep. is ACO (Y/N): N

Defense priority rating : N/A

N/A supplemental sheet

Equipment title vests with: Sponsor X

GIT

Administrative comments -

PROJECT INITIATION. E.I. DUPONT TERMS AND CONDITIONS AS SPECIFIED IN OCA
1-82 REV. 1985 MODIFIED BY GTRC LETTER DATED 9/27/85



182
K529

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Date 9/13/89

Project No. E-25-619

Center No. R6596-OAO

Project Director G. G. Eichholz

School/~~XXX~~ ME

Sponsor E. I. duPont de Nemours & Company

Contract/Grant No. P.O. AX0857216

GTRC X GIT

Prime Contract No. DOE AC09-76SR00001

Title Absorption of Actinides on SRP Soil

Effective Completion Date 6/2/89 (Performance) 6/2/89 (Reports)

Closeout Actions Required:

☐ None

☐ Final Invoice or Copy of Last Invoice

☐ Final Report of Inventions and/or Subcontracts Ques. sent to PI

☐ Government Property Inventory & Related Certificate

☐ Classified Material Certificate

☐ Release and Assignment

☐ Other

Includes Subproject No(s).

Subproject Under Main Project No.

Continues Project No.

Continued by Project No.

Distribution:

☐ Project Director

☐ Administrative Network

☐ Accounting

☐ Procurement/GTRI Supply Services

☐ Research Property Management

☐ Research Security Services

☒ Reports Coordinator (OCA)

☒ GTRC

☒ Project File

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☐ Other



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October 19, 1988

Please reply to:

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ATLANTA, GEORGIA 30332 U.S.A.

Dr. P. McIntyre
Advanced Waste Management Division
Savannah River Laboratory
Aiken, South Carolina 29808-0001

Monthly Progress Report - Our Project E25-619

Dear Dr. McIntyre:

Contractual arrangements for this project have finally been completed and we have started work. We are characterizing some soil samples at hand that came originally from the SRP waste disposal area and have been used in earlier work for your division. If you want us to use soil from other locations, please let us know.

My principal concern is the availability of suitable tracers. We have located about 1.3 mCi of Np-237 here, which we expect to use, as well as some uranium. It would be helpful, if you could obtain 0.2-1 mCi samples of Am-241, Cm-242 and possibly Np-235 from available supplies at SRP, as they may be difficult to find elsewhere.

Please call me at 404-894-3722, if you have any questions.

Yours truly,

G. G. Eichholz
Regents' Professor

GGE/bc

cc: P. Heitmuller (OCA)
R. F. Dawkins (ME)

E-25-619



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November 22, 1988

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Dr. P. McIntyre
Advanced Waste Management Div.
Savannah River Laboratory
Aiken, SC 29808-0001

Monthly Progress Report - Our Project E25-619

Dear Dr. McIntyre:

Since the previous letter, we have completed characterization of soil samples. We expect to measure surface absorption of CS-137, as a reference case both in beaker samples and in columns as soon as we obtain a new supply of tracer solution. After that we expect to proceed to actinide tracers, using the Np-237 we have at hand.

We would still be interested to know if you have located appropriate actinide tracers at SRP. I expect to be at SRP December 13-14 and hope to have a chance to touch base with you.

Yours sincerely,

G. G. Eichholz
Regents' Professor

GGE:cv

cc: P. Heitmuller (OCA)
R. F. Dawkins (ME)



Georgia Institute of Technology

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January 24, 1989

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ATLANTA, GEORGIA 30332 U.S.A.

Dr. P. T. McIntyre
Advanced Waste Management Division
Savannah River Laboratory
Aiken, SC 29808-0001

Project E25-619

Dear Dr. McIntyre:

Progress has been rather slow over the Christmas break, but we are fully back in action now. We have received fresh Cs-137 solution and are in the process of baseline sorption tests using it.

I tried several times to reach you in the interval and I would still be interested to find out if we could obtain microcuries amounts of Pu-238 or 237 or of Am-241 from SRP stock. Please let me know if there is such a possibility.

Yours truly,

G. G. Eichholz
Regents' Professor Emeritus

GGE/bc
cc: P. Heitmuller (OCA)
R. F. Dawkins (ME)

ADSORPTION OF ACTINIDES ON SRP SOIL

Final Report

Contract No. AX-0857216
Our Project No. E25-619

Geoffrey G. Eichholz
Principal Investigator

To: Interim Waste Technology Division
Savannah River Laboratory
Westinghouse Savannah River Co.

Nuclear Engineering and Health Physics Programs
Georgia Institute of Technology
Atlanta, Georgia 30332

July 1989

ABSTRACT

The purpose of this project was the determination of the specific soil adsorption coefficient, K_d , of selected soil materials from the Savannah River Site for various dissolved actinides in soil-equilibrated water using batch-type and column measurements.

The outcome of this work has unfortunately been disappointing, mainly due to two causes: the long delay in awarding the contract, which resulted in the loss of the key researcher early on due to graduation and departure, and because of difficulties in obtaining appropriate tracer materials from DOE facilities or commercial suppliers. Consequently, only very limited data have been obtained.

PROJECT STAFF

Geoffrey G. Eichholz, Ph.D.

Principal Investigator

Christopher Aguilera, B.S.

Graduate Research Assistant

Won-jae Park, M.S. H.P.

Graduate Research Assistant

INTRODUCTION

The movement of long-lived fission products and transuranium elements through the soil underlying the Savannah River site has been of continuing concern over many years and several aspects have been studied at Georgia Tech (1-4). Particular attention has been paid to trace quantities of transuranium elements that might be leached from waste disposal trenches and King (5) has drawn attention to the potential impact of neptunium migration. Even though NCRP estimates of the toxicity of neptunium have been scaled down in the most recent report (6), it is still important to evaluate the mobility of Np and the other transuranium alpha emitters under actual conditions at the Savannah River site.

The principal retardation mechanism for dissolved ions for migration through soil is by ion exchange retention on clay minerals, which are abundant at the Savannah River site. This process is a dynamic one and the effective retardation is highly site-specific, as it depends on effective surface area, flow velocities and the nature and concentration of competing dissolved ions. For plutonium, Cleveland (7,8) has shown, how much the measured adsorption rates depend on the water characteristics and plutonium species present. In particular, he has shown the significant differences observed in comparing Pu species, Pu III, IV and (V + VI), in deionized water and in contact with various mineral types. (7,9)

The usual method of describing the effective adsorption on "representative" mineral samples is in terms of the distribution coefficient K_d or the retardation factor R_d . Methods for determining the factors have been described by Rai and Serne (10) and R_d values for various fission products and actinides have been tabulated by Serne and Relyea (11). For americium and strontium, R_d values were tabulated that varied over three orders of magnitude. Similarly, they list widely varying values for exchangeable

plutonium, but at pH4 and for non-standardized surface area conditions. Similar observations have been published by Allard (12) for actinides in igneous rocks.

PROPOSED PROCEDURE

In order to test conditions of migration for SRS waste realistically, it was considered important to simulate adsorption under conditions closely resembling the site-specific ones. This involved using soil material from the site and soil-equilibrated water. Previous test work (3,4) has resulted in characterization of various SRS soil samples, showing appreciable differences in characteristics. However, for the present purpose it was felt to be adequate to select one of those soil samples. Similarly, the water used had to be equilibrated by contact in deionized water with that soil over an extended period, though it proved impractical to control or monitor oxygen content.

The proposed procedure consisted of two types of contact operations:

- a. batch tests involving sized soil samples in contact with labeled solutions, made up of either deionized water or soil equilibrated water; and
- b. flow tests, using packed soil columns of a type used in previous test work (4), again with two types of labeled solutions.

The systems would be standardized with Cs-137 solutions, to test reproducibility of conditions and to measure the effective surface area of the soil material.

Proposed actinide tracers included Np-235, Am-241 and Pu-237; however, difficulties were encountered in obtaining trace solutions for this work and in the end only a weak americium solution was available.

For the flow tests, a number of Lucite columns, 3 cm ID, 15 cm in length, with O-ring closure at top and bottom were constructed. Packing of the columns followed previous procedures (3) to minimize air bubbles and channeling. However, because of source unavailability, these columns were not utilized in the end.

RESULTS OF TEST WORK

Soil Characterization

A composite sample, similar to "SRP #3 soil" used previously was selected for these tests and designated SRP #4. A screen analysis was performed and the soil was characterized, on a 100g sample, using the U.S. Department of Agriculture Soil Classification criteria. Table 1 lists the resulting data.

Table 1		
Soil Classification - SRP #4		
Particle	US DA Size	SRP %
Silt	0 - 2 μm	} 24.82
Clay	2 - 50 μm	
Very fine sand	50 - 100 μm	~12.70
Fine sand	0.1 - 0.25 μm	~13.68
Medium sand	0.25 - 0.5 μm	19.46
Coarse sand	0.5 - 1 μm	24.46
Very coarse sand	1 - 2 μm	4.39

Surface area determination was performed using the EGME (ethylene glycol monoethyl ether) technique (13). About 1g of soil was placed into tared planchets and treated with approximately 3 ml of EGME. The planchets were placed into a desiccator, which was then evacuated. The soil was weighed and reweighed until the mass stabilized. This mass was used in the determination of soil surface area. The initial mass was subtracted from the final mass to determine the amount of EGME absorbed onto the soil surface. This mass was then divided by a conversion factor to determine the surface area. The surface area correction factor was 0.000286 g/m².

Three samples were studied and the results were:

<u>Sample</u>	<u>Mass EGME Retained Per Gram Soil</u>	<u>Surface Area Per Gram Soil</u>
1.	0.0273 g	99.9 m ²
2.	0.0249 g	86.9 m ²
3.	0.0207 g	72.3 m ²

$$\text{Average surface area} = 84.9 \text{ g/m}^2 \pm 11.7 \text{ g/m}^2$$

This value was used in the tracer absorption studies.

Preparation of Water Samples

Three samples of deionized water were mixed with soil to simulate ground water at the SRP site. This was achieved by mixing large samples of water in the following proportions.

Sample 1 0.167 g soil/ml water

Sample 2 0.33 g soil/ml water

Sample 3 1 g soil/ml water

This equilibrated water was used in the absorption studies after the pH had stabilized.

Table 2 lists the approach to steady-state condition with test samples taken over a 2-month period. It should be noted that the deionized water sample also changed with time, presumably to the CO₂ uptake from the air. The samples were swirled gently from time to time.

TABLE 2
pH Measurements on Soil-Water Mixtures

Successive Trials	Deionized Water	Sample 1	Sample 2	Sample 3
1	6.73	4.96	5.04	4.80
2	6.22	5.19	4.93	4.80
3	5.68	4.80	4.75	4.70
4	5.80	4.85	4.74	4.72
5	6.14	5.16	5.06	4.96
6	5.91	4.89	4.69	4.62
7	6.31	5.30	4.82	4.63
8	6.38	4.94	4.58	4.58
9	8.15	4.48	4.67	4.59
10	5.87	4.80	4.54	4.36
11	5.65	4.70	4.64	4.69
12	5.65	4.67	4.64	4.60
13	5.69	4.69	4.63	4.61
14	5.66	4.74	4.66	4.63
15	5.49	4.66	4.59	4.60

Note the relatively low pH value for the SRP #4 soil waters.

Cesium-137 Adsorption Tests

A 5 millicurie Cs-137 source was purchased to serve as a stock solution. The source consisted of CsCl in 0.5N HCl and was diluted initially in 10 ml of deionized water. Aliquots were withdrawn by syringe as needed to provide sample solutions.

To calibrate the sodium iodide well counter employed, a reference Cs-137 solution was counted under reproducible conditions. Using 150 channels of a 1096-channel analyser, background was found to be 6.84×10^{-3} cps/channel. Using a source of known activity, the effective efficiency of the detector, (intrinsic efficiency x geometry), was found to be 3.7%.

The stock solution was counted in this geometry to determine the activity of the stock solution.

Sample: 1 ml 500g 150 ch. under peak

<u>Counts</u>	<u>Avg cps</u>	<u>Background for 150 ch.</u>	<u>Net cps</u>	<u>Net dps</u>
83072				
84133	168.3 cps	1.02 cps	167.3 cps	4520.89
85173				

Net activity per unit volume = $0.122 \mu\text{Ci/ml}$

Separation of soil and solution was obtained by centrifuging and decanting of the liquid. The soil sample was then counted, still within the centrifuge tube, in order to minimize transfer losses.

To obtain a background reading for this geometry, 2g of soil were placed in the centrifuge tube and 10 ml of water (deionized) were put in the tube. The tube was then centrifuged and the supernatant was poured off. Counts were then taken to obtain a background for the test conditions.

<u>Trial (140 ch)</u>	<u>Counts in 1000 s</u>	<u>Avg cps/ch</u>
1	2361	
2	2319	0.0106
3	2927	

1 ml of stock solution was then counted in a centrifuge tube to determine a centrifuge tube geometry.

1 ml solution in 15 ml centrifuge tube placed in the well-type detector. 500g counts.

<u>Counts</u>	<u>Avg cps</u>	<u>Background (150ch)</u>	<u>net cps</u>
241,168			
239,586	479.45	1.02 cps	478.43
238,428			

Activity of 1 ml solution = $(0.122 \times 10^{-6} \text{ Ci}) (3.7 \times 10^{10} \text{ cps/ci}) = 4514 \text{ dps}$

Efficiency of centrifuge tube geometry = $0.1060 = 10.6\%$.

Cs-137 Beaker Tests

For the beaker tests ~2g of soil were placed in centrifuge tubes and varying concentrations of tracer were placed in the tube to make up 10 ml and shaken in a wristaction shaker. After about 15 minutes the samples were centrifuged and the supernatant poured into a separate centrifuge tube for analysis. The tube was tared with soil and the dry weight was subtracted from the net weight to get the mass of remaining supernatant in the tube after the absorption test. The wet centrifuge tube was then counted. This gives gross counts due to absorption onto the soil of the tracer, activity remaining in the tube due to the supernatant, and background.

To find the net activity absorbed on the soil, take the gross cps from the "wet" centrifuge tube, subtract the activity from the remaining supernatant and subtract background. The net count rate obtained was then used to find the amount of activity absorbed onto the soil. Since the surface area per unit mass was known, one can determine the activity absorbed per unit area. This quantity is then divided by the initial activity per unit volume of the tracer to obtain a K_d value.

Table 3 shows the test results obtained by counting separately the moist soil and the supernatant water for 500 seconds each.

Table 3: Cs-137 Adsorption: Deionized Water

Sample #	Mass of Sample (g)	Volume of Tracer Added	Gross Counts		Counts of 1 ml Remaining (SN)	120 ch Background Counts/sec
			Soil + Remaining Supernatant (SN)	Volume Remaining Supernatant (ml)		
1	1.999	0.3 ml tracer to 9.7 ml deionized H ₂ O	59,003	0.647	1045	1.27
			60,000		1182	
			59,741		956	
2	2.000	0.4 ml tracer to 9.6 ml deionized H ₂ O	76,612	0.700	1416	1.27
			77,520		1385	
			77,595		1348	
3	2.076	0.5 ml tracer to 9.5 ml deionized H ₂ O	99,414	0.579	1401	1.27
			99,194		1492	
			99,527		1528	
4	2.000	0.6 ml tracer to 9.4 ml deionized H ₂ O	112,875	0.763	2568	1.27
			115,145		2453	
			114,679		2448	
5	2.001	0.7 ml tracer to 9.3 ml deionized H ₂ O	191,705	0.723	1432	1.27
			190,715		1385	
			190,868		1506	

Table 4 shows the distribution coefficient K_d and the retardation factor R_d obtained from these results. The five runs were fairly reproducible.

Table 4		
Sample	$K_d \left(\frac{\frac{\mu Ci}{m^2}}{\frac{\mu Ci}{m\ell}} \right)$	$R_d = \left(1 + \frac{1}{K_d} \right)$
1	4.83×10^{-2}	$21.7 \text{ m}^2/\text{m}\ell$
2	4.67×10^{-2}	22.4
3	4.59×10^{-2}	22.7
4	4.60×10^{-2}	22.7
5	5.20×10^{-2}	20.2
		21.9 Avg.

Similar tests were performed with soil-equilibrated water after restandardizing the stock solution. Table 5 shows the results obtained with 500 sec. count times. The pH of all solutions was monitored and found to vary little.

Table 6 again shows the calculated values of K_d and R_d .

Table 5: Cs-137 Adsorption: Soil Equilibrated Water

Sample #	Mass of Sample (g)	Tracer Added (ml)	Gross Counts Soil + Remaining Supernatant (SN)	Volume Remaining Supernatant (ml)	Gross Counts of 1 ml Remaining (SN)	Backed in cps
1	2.007	0.3 ml tracer to 9.7 ml equilibrated water	51,767 51,890 51,881	0.829	2871 2946 2963	1.38
2	2.003	0.9 ml tracer to 9.5 ml equilibrated water	93,722 93,830 93,761	0.799	3107 3205 3225	1.38
3	1.996	0.6 ml tracer to 9.4 ml equilibrated water	108,515 102,544 105,105	0.645	3497 3768 4107	1.38
4	2.004	0.7 ml tracer to 9.3 ml equilibrated water	138,379 145,525 143,940	0.746	2760 2834 2699	1.38

Table 6: Cs-137 Retardation on SRP #3 Soil

Sample	$K_d \left[\frac{\frac{\mu\text{Ci}}{\text{m}^2}}{\frac{\mu\text{Ci}}{\text{m}\ell}} \right]$	$R_d \text{ (m}^2/\text{m}\ell)$
1	3.86×10^{-2}	26.9
2	4.26×10^{-2}	24.5
3	4.02×10^{-2}	25.9
4	4.69×10^{-2}	22.3
		<hr/> 24.9 Avg.

As expected the K_d values are somewhat lower for soil-equilibrated water and the R_d value higher, by about 13.7%.

Actinide Tests

A weak solution of Am-241, of the order 35 nCi, was obtained from material at hand. This proved to be insufficient to allow positive adsorption tests on the soil samples, when used as a stock solution.

A neptunium-237 source at hand at Georgia Tech, that we had expected to use, became unavailable at a later date as there was reluctance to dissolve it and use it in solution form.

Various attempts to obtain Pu and Np tracer solutions from Savannah River Laboratory and Argonne National Laboratory were fruitless.

CONCLUSIONS

The work described did not accomplish its main objective due to difficulties in obtaining actinide tracer solutions.

For cesium-137 it was shown that, for the SRS soil samples used, there was a 13.7% difference in soil adsorption between deionized water and soil-equilibrated water. Such differences must be taken into account when modeling subsurface migration.

REFERENCES

1. G. G. Eichholz. Radionuclide Migration in the SRP Lysimeters. Final Report, Project E26-627, to Savannah River Laboratory, 1984.
2. G. G. Eichholz, Transport Model for Radionuclide Migration in the SRP Lysimeters. Final Report, Project E25-606, to Savannah River Laboratory, 1986.
3. G. G. Eichholz and J. Whang. Waste Migration in Shallow Burial Sites under Unsaturated Flow Conditions. Proc. Waste Management 87, 3, 219-226 (1987).
4. G. G. Eichholz, M. F. Petelka and J. Whang. Leaching and Migration of Low-level Wastes under Unsaturated Conditions. Radioactive Waste Management and the Nuclear Fuel Cycle, (in press).
5. C. M. King and E. L. Wilhite. Alpha Contaminated Waste Management and Environmental Impact at the Savannah River Plant. DP-MS-82-83 (1982)
6. Neptunium: Radiation Protection Guidelines. NCRP Rept. No. 90, National Council on Radiation Protection and Measurements, Bethesda, MD, 1988.
7. J. M. Cleveland, T. F. Rees and K. L. Nash. Plutonium Speciation in Selected Basalt, Granite, Shale and Tuff Groundwaters. Nucl. Technol. 62, 298-310 (1983)

8. J. M. Cleveland. The Chemistry of Plutonium. American Nuclear Society, LaGrange Park, IL, 1979.
9. R. C. Routson, G. Jansen and A. V. Robinson. ^{241}Am , ^{287}Np and ^{99}Tc Sorption on Two U.S. Subsoils from Differing Weathering Intensity Areas. Health Phys. **33**, 311-317 (1977).
10. D. Rai and R. G. Serne. Methods for Determining Radionuclide Retardation Factors: Status Report. DOE Rept. PNL-3349, Pacific Northwest Lab., 1980.
11. R. J. Serne and J. F. Relyea. The Status of Radionuclide Sorption - Desorption Studies Performed by the WRIT Program, in The Technology of High-level Nuclear Waste Disposal (Vol. 1), DOE/TIC-4621 (Vol. 1) Techn. Information Center, U.S. Dept. of Energy, 1981.
12. B. Allard, G. W. Beall and T. Krajewski, The Sorption of Actinides in Igneous Rocks. Nucl. Technol. **49**, 474 - 480 (1980).
13. D. L. Carter, M. D. Heilmann and C. L. Gonzalez. Ethylene Glycol Monoethyl Ether for Determining Surface Area of Silicate Minerals. Soil Sci. **100**, 356-360 (1965).